Journal of Lake and Reservoir Management 14(2-3):266-277, 1998

Chemical Exchange at the Sediment-Water Interface of Cannonsville Reservoir

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ABSTRACT

Erickson, M. J. and M. T. Auer. 1998. Chemical exchange at the sediment-water interface of Cannonsville Reservoir. Lake and Reserv. Manage. 14(2-3):266-277.

Rates of chemical exchange at the sediment-water interface of Cannonsville Reservoir were determined using intact sediment cores. Reference sites for coring were selected based on the results of a surficial sediment survey. Higher levels of volatile suspended solids, chemical oxygen demand, total organic carbon, total nitrogen, and total phosphorus were noted at deep water stations proximate to the dam and near the discharge of the West Branch of the Delaware River (WBDR, the reservoir's major tributary). Rates of sediment oxygen demand (SOD), measured at 20 °C at the three reference sites, ranged from 0.66 to 1.67 $gO_2 \cdot m^{-2} \cdot d^{-1}$ with a mean ± s.d. of 1.06±0.23 $gO_2 \cdot m^{-2} \cdot d^{-1}$. No statistically significant variation in SOD with location in the reservoir was noted. No phosphorus (P) release was detected under aerobic conditions. Rates for cores incubated under anaerobic conditions ranged from 9.2 to 15.6 $mgP \cdot m^{-2} \cdot d^{-1}$, with a reservoir-wide mean ± s.d. of 12.9 ± 2.2 $mgP \cdot m^{-2} \cdot d^{-1}$. P-release rates at P-enriched sites (surficial sediment survey) were higher than at mid-reservoir locations with lower sediment-P. Rates of ammonia-nitrogen (NH_3-N) release ranged from 19.6 to 43.2 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$ with a reservoir-wide mean ± s.d. of 31.8 ± 7.2 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$. A general trend of decreasing sediment NH_3-N release with distance from the discharge of the WBDR was noted. Rates of sediment exchange measured here are consistent with those reported for other systems of a similar degree of nutrient enrichment and trophic state. Downcore profiles of sediment chemistry suggest that while organic carbon and nitrogen are undergoing diagenesis in the reservoir (SOD is exerted and NH_3-N release is observed), P deposited to the sediment remains in the particulate form and is not recycled. The sediments are, however, rich in the forms of particulate P which support release. High rates of P exchange may be expected if trophic state conditions deteriorate further, resulting in extended anoxia.

Key Words: ammonia, phosphorus, reservoirs, sediments, water quality..

As the repository for a substantial fraction of the non-conservative materials entering a lake or reservoir, surficial sediments can play a significant role in mediating water quality. Sediments become enriched in nutrients and organic matter as algal biomass and allochthonous particulate materials are delivered to the bottom. Decomposition of sedimented organic matter leads to dissolved oxygen (DO) depletion and the release of nitrogen (N) and phosphorus (P) to the water column. These processes can have dramatic effects on water quality. Sediment oxygen demand (SOD) often plays a major role in the oxygen budget of eutrophic lakes and reservoirs, contributing significantly to overall hypolimnetic oxygen consumption (e.g., 25% in Hamilton Harbor, Lake Ontario, Snodgrass and Ng 1985; 42% in Lake Erie, Adams et al. 1982; and > 72% in Onondaga Lake, Gelda et al. 1995). N and P released from the sediments may be transported to the surface waters, further enhancing levels of primary production (Chapra and Reckhow 1983). Sediment ammonia (NH_3-N) release is of additional concern because of potential toxicity effects and because the microbially-mediated conversion of ammonia to nitrate consumes DO (Chapra 1997). Chemical exchange at the sediment-water interface has the potential to retard a waterbody's response to management efforts. For example, sediment P release has been observed to persist for extended periods following reductions in external P loads (e.g., Lake Norrviken, Sweden, Ahlgren 1977; Shagawa Lake, USA, Larsen et al. 1981; Lake Sammamish, USA, Welch et al. 1986; and Lake Varese, Italy, Rossi and Premazzi 1991).

Material or mass balances are often conducted as a first step in developing lake restoration programs. Quantification of rates of chemical exchange is an important component of this analysis. Rates may vary significantly among and also within systems due to a number of environmental factors and thus site-specific determination of rates is necessary. Methods applied to quantify chemical exchange at the sediment-water interface include: (1) whole lake mass balance calculations (e.g., Dillon and Rigler 1974); (2) estimation from profiles of sediment chemistry (e.g., Berner 1980, Enell and Löfgren 1988, Penn 1994) and (3) direct measurement (e.g., Kamp-Nielsen 1974, Freedman and Canale 1977, Auer et al. 1993). While it has been shown that release rates may be accurately estimated from profiles of sediment chemistry and through mass balance calculations, direct measurement remains the most reliable approach.

The research reported here describes field and laboratory studies characterizing spatial variation in sediment chemical composition and quantifying rates of chemical exchange at the sediment-water interface. Specifically, we report the results of a surficial sediment survey, laboratory measurements of SOD and rates of NH_3-N and P release, and sediment profiles of selected analytes related to SOD and nutrient cycling. The surficial sediment survey serves a screening function, identifying regions of similar chemical composition and degree of nutrient enrichment for further study (cf. Auer et al. 1996). Cores representative of individual sediment regions are then utilized in developing profiles of sediment chemistry and in the determination of SOD and rates of NH_3-N and P release. The rates of chemical exchange measured at these sites may then be applied over regions of common physicochemical character in conducting mass balance analyses. The results presented here may also be of value in estimating the timing and magnitude of the reservoir's response to remediation efforts. This is the "when and to what extent" question posed by Cooke et al. (1993) in their treatise on lake and reservoir management. The role of sediments in mediating that response is best addressed by integrating the program of field and laboratory studies within the framework of a mathematical model of reservoir water quality (Doerr et al. 1998; cf. Auer and Canale 1986).

Study Site

Cannonsville Reservoir is the third largest and most eutrophic of the 19 reservoirs which comprise the New York City (NYC) drinking water supply system (see Effler and Bader 1998 for a review of reservoir morphometry). The reservoir is fed by the West Branch of the Delaware River (WBDR; draining 79% of the reservoir's 1160 km² watershed), Trout Creek (draining 5% of the watershed) and several smaller tributaries (Owens et al. 1998). Cannonsville Reservoir has been in operation since 1965. Because development in the watershed is modest, it is assumed that the reservoir is in equilibrium with its external loading. Eutrophic over its entire length, substantial gradients in water quality-related parameters nonetheless exist along the major axis of the reservoir (Effler and Bader 1998). These gradients exist largely in response to inputs from WBDR, the major source of suspended sediment and nutrients (Longabucco and Rafferty 1998). These gradients, as well as those observed for particle settling velocities and sediment flux (Effler and Brooks 1998), suggest a potential for spatial heterogeneity in surficial sediment character. Sediment resuspension occurs in the reservoir, although the extent to which deep water sediments participate in this phenomenon remains unresolved (Effler et al. 1998a). Observations of summer DO depletion in the reservoir's hypolimnion (Effler and Bader 1998) suggest that chemical exchange at the sediment-water interface may be a potentially important feature of the system's limnology.

Methods and Materials

A surficial sediment survey was conducted to define regions within the reservoir having similar physicochemical characteristics. Sampling sites were identified within those regions where sediment cores could be collected for further study. Cores were then utilized for laboratory measurement of chemical exchange at the sediment-water interface and in the development of profiles of sediment chemistry.

Surficial Sediment Survey and Sediment Core Collection

Surficial sediment samples were collected from five sites along the main axis of the reservoir and from one site in the Trout Creek arm (Fig. 1) on 21-22 September 1994 using a PONAR dredge. These sites correspond to those adopted for water column studies during 1995 (Effler and Bader 1998, Effler and Brooks 1998, Effler et al. 1998b). Surficial sediment samples were placed in glass jars, sealed, labeled, placed on ice and transported to the laboratory at Michigan Technological University where they were stored at 4 °C. Subsamples from each site were analyzed in triplicate for a suite of physical and chemical parameters (Table 1).

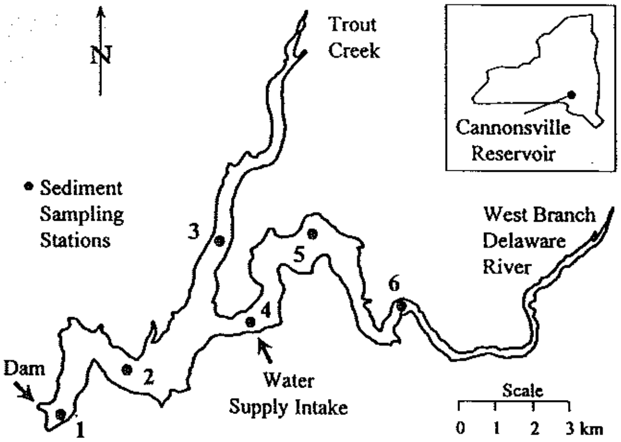

Figure 1.–Sampling sites on Cannonsville Reservoir.

Intact, undisturbed replicate sediment cores were collected from three sites identified through the surficial sediment survey as being representative of regions of common chemical character. Coring sites were located near the deepest point in the reservoir's cross section at positions likely to represent depositional basins. Cores were collected on 5-6 July and 29-30 August 1995 using a Jenkins core sampler fitted with (6.2- x 50-cm) lexane core liners. Upon retrieval, each core liner contained approximately 15 cm of sediment and 35 cm of overlying water. Cores (sediment and overlying water) were inspected for disturbance at the sediment-water interface, sealed, and packed in ice in covered containers for transport to the laboratory. The cores were stored in the dark at 4 °C until further processed or until utilized in chemical exchange experiments (within 10 to 14 days following collection). Water was collected from the reservoir's hypolimnion on each sampling date for use in chemical exchange experiments. The water was passed through a glass fiber filter (Whatman 934-AH) to remove plankton and stored in the dark at 4 °C.

Sediment Oxygen Demand Measurement

Laboratory respirometry, a direct measurement technique, has been frequently applied for estimation of SOD in deep water systems where an *in situ* approach is impractical (Gardiner et al. 1984, Whittemore 1986, Fowler et al. 1987, Gelda et al. 1995, Truax 1995). Here, a respirometric approach similar to that used by Gardiner et al. (1984) and Gelda et al. (1995) was employed, where the time rate of change in DO concentration in the water overlying the sediment was measured with an oxygen electrode. Replicate measurements were made on three cores collected in July and one core collected in August.

Prior to each replicate measurement, the water in the core liner (Fig. 2) was drawn down to a height of ~5 cm above the sediment and the core liner refilled

Table 1.–Analytical methods. Analysis applied in: (a) exchange experiments, (b) surficial sediment survey, and (c) sediment profiles.

Parameter	Technique	Reference
Ammonia nitrogen[a]	Spectrophotometric; phenol hypochlorite	Solorzano 1969; Brooks 1989
Calcium carbonate[b]	Gravimetric	Dean and Gorham 1976
Chemical oxygen demand[b]	Ferrous ammonium sulfate	APHA 1985
Clastics[b]	Gravimetric	Dean and Gorham 1976
Moisture content[b]	Gravimetric	APHA 1985
pH[a]	Electrode	APHA 1985
Phosphorus fractions[c]	Sequential chemical extractions	Penn et al. 1995
Soluble reactive phosphorus[a]	Spectrophotometric; ascorbic acid	APHA 1985
Total nitrogen[b,c]	CHN analyzer	Hedges and Stern 1984
Total organic carbon[b,c]	CHN analyzer	Hedges and Stern 1984
Total phosphorus[b,c]	Persulfate digestion – unfiltered	APHA 1985
Volatile solids[b]	Gravimetric	APHA 1985

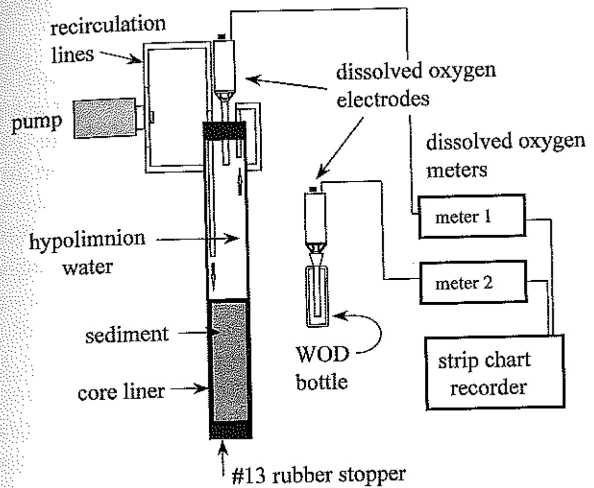

Figure 2.–Experimental apparatus for SOD measurements.

(no headspace) with aerated, re-filtered (0.45-µm cellulose acetate) hypolimnion water. The initial DO in these experiments ranged from 6 to 10 mg · L^{-1}; preliminary studies revealed no dependency of SOD on DO over a range of 2 to 9 mg · L^{-1}. The core liner was capped with a 3-hole stopper holding an Orion DO probe (Model #97-08) and inlet and outlet tubes connected to a pump (FMI Model RHV-0) fitted with a stroke rate controller (FMI Model V-100; Fig. 2). The pump was used to circulate the water through the inlet and outlet tubes and over the sediment, minimizing oxygen concentration gradients at the sediment-water interface. The inlet tube was fixed at a height of ~8 cm above the interface to avoid disturbance of the sediment-water interface. The water recirculation rate required to maintain complete mixing was determined by observation of the movement of fine suspended material in separate test cores. The inlet and outlet tubes were autoclaved between trials to prevent development of oxygen-demanding bacterial films on their inner walls. A second DO probe was placed in a 300-ml glass bottle containing oxygenated, re-filtered hypolimnion water to determine the water oxygen demand (WOD). SOD and WOD incubations were carried out in the dark at 8 °C, a representative summer average hypolimnion temperature for Cannonsville Reservoir (Owens 1998). DO concentrations in the water overlying the sediment and in the WOD bottle were recorded concurrently using a strip chart recorder. Measurements were made for a minimum of 12 hours, achieving a stable, linear response of DO versus time. SOD ($gO_2 \cdot m^{-2} \cdot d^{-1}$) was calculated as the time rate of oxygen depletion in the water overlying the sediment ($gO_2 \cdot d^{-1}$), minus the WOD ($gO_2 \cdot d^{-1}$), divided by the surface area of the sediment (m^2) in the core liner.

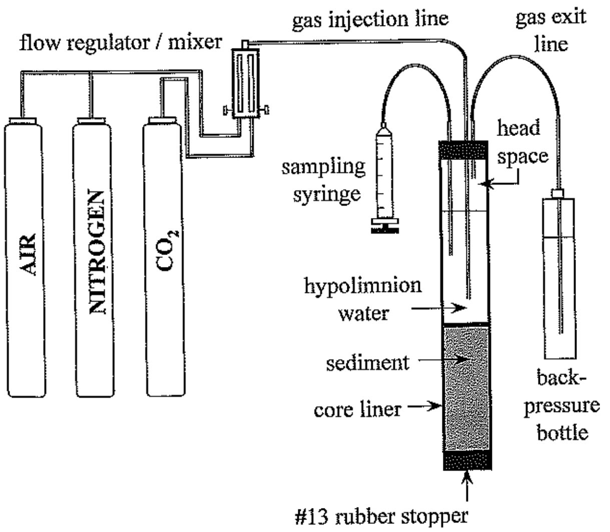

Figure 3.–Experimental apparatus for ammonia-nitrogen and phosphorus release rate measurements.

Release Rate Measurements

Rates of NH_3-N and P release were measured in the laboratory on intact cores (Fig. 3). The experimental approach, monitoring P and NH_3-N accumulation in the water overlying the sediment, was in the spirit of studies by Kamp-Nielsen (1974), Auer et al. (1993), and Penn (1994). Conditions of pH (6.7), temperature (8 °C) and DO in the water overlying the sediments were maintained at levels representative of the reservoir's hypolimnion (Effler and Bader 1998, Owens 1998) as described below. P-release was measured under aerobic and anaerobic conditions to examine differences in rates associated with the oxygen depletion typical of summer stratification (redox effects). NH_3-N release was measured only under anaerobic conditions to eliminate the effects of nitrification. Aerobic phosphorus release rate measurements were made on cores collected in triplicate from each of the three sampling sites in July and August. Anaerobic P release and NH_3-N release experiments were conducted on cores collected in triplicate at each of the three sampling sites in August.

Cores used for the experiments contained approximately 15 cm of sediment, 15 cm of overlying water, and 20 cm of headspace. At the start of the experiment, the overlying water was drawn down to a depth of ~5 cm above the sediment and replaced to a depth of 15 cm (450 mL) with filtered (Whatman 934-AH) hypolimnetic water (deoxygenated to avoid sudden exposure of anaerobic sediment to oxygen). The cores were capped with a rubber stopper fitted with gas inlet and outlet lines and a sampling line connected to a 100-mL syringe. The caps were sealed with a silicone sealant to prevent oxygen diffusion into anaerobic cores, and the gas outlet lines were placed under water to insure a positive pressure inside the core liner, preventing the introduction of oxygen in the event of gas flow interruption. DO and pH levels were maintained by gently bubbling a mixture of N_2 and CO_2 (anaerobic environment) or CO_2 and air (aerobic environment) through the overlying water. The gas inlet line was positioned approximately 8 cm above the sediment-water interface. Gas flow further served to eliminate chemical concentration gradients in the water column. The pH and DO were monitored in a parallel control core, and pH was adjusted by varying the ratio of N_2:CO_2 or air:CO_2. Minimal adjustment was required.

Cores were incubated for 50 days and 100-mL samples were withdrawn (syringe) at 4- to 5-day intervals for analysis. The volume lost through sampling was replaced with NH_3- and P-free synthetic reservoir water (Table 2) to maintain an ion balance comparable to that of the reservoir. The samples were filtered (0.45-µm cellulose acetate membrane) and frozen in acid-washed, 250-mL glass bottles until analyzed (Table 1) for soluble reactive phosphorus (SRP) and NH_3-N. Paired determinations of soluble reactive (SRP) and total dissolved phosphorus (TDP; Table 1) made on selected samples indicated that SRP accounted for more than 95% of the phosphorus released. The rate of NH_3-N and P accumulation ($mg \cdot d^{-1}$) was determined by least squares, linear regression of the observed mass of SRP or NH_3-N in the overlying water, corrected for the amount removed through sampling. Fluxes ($mg \cdot m^{-2} \cdot d^{-1}$) were calculated by dividing the rate of accumulation by the surface area of the sediment (m^2).

Profiles of Sediment Chemistry

Cores used to develop chemical profiles were sliced (0.5-, 1.0- and 2.0-cm increments), and each slice was divided into two subsamples. One subsample was weighed and dried for dry weight determination and chemical analysis (total nitrogen, TN; total phosphorus, TP; and total organic carbon, TOC; Table 1). The other subsample was placed in a 40-mL borosilicate glass vial, the headspace purged with N_2 gas and the vial sealed and stored at 4 °C for analysis of P fractions. A sequential chemical extraction procedure (Table 1) was applied to partition the P contained in the sediment into one of four operationally defined fractions: iron-aluminum-P, organic-P, calcium mineral-P, and refractory-P. Penn et al. (1995) used these fractions to define the labile P fraction in lake sediments, i.e., that ultimately available for recycle and release. Here, we utilize estimates of the labile fraction to consider the potential for P release in Cannonsville Reservoir sediments.

Results and Discussion

Surficial Sediment Survey

Levels of chemical oxygen demand (COD), volatile suspended solids (VSS), calcium carbonate ($CaCO_3$), clastics, TOC, TN, and TP were determined for the surficial sediment of Cannonsville Reservoir (Table 3).

Table 2.–Ionic composition of actual and synthetic reservoir water.

Ion	Actual Reservoir Water ($\mu eq \cdot L^{-1}$) [a]	Synthetic Reservoir Water ($\mu eq \cdot L^{-1}$)	Salt Added	Final Concentration ($mg \cdot L^{-1}$)
Na^+	161	160	$CaSO_4$	4.1
K^+	26	25	$MgSO_4$	7.5
Ca^{+2}	328	335	$CaCO_3$	13.8
Mg^{+2}	143	145	$MgCl_2 \cdot 6H_2O$	2.0
Cl^-	170	175	$NaNO_3$	2.6
NO_3^-	29	30	NaCl	7.6
HCO_3^-	242	275	KCl	1.9
SO_4^{-2}	183	185		

[a] New York City, Department of Environmental Protection, unpublished data.

Table 3.–Results of surficial sediment survey.

Site	COD	VSS	$CaCO_3$	Clastics	TOC	TN	TP
1	97	9	4	87	2.9	0.38	0.20
2	83	8	4	88	3.3	0.37	0.22
3	55	6	3	91	1.6	0.14	0.14
4	48	5	3	92	1.3	0.19	0.14
5	51	7	3	90	2.5	0.27	0.16
6	77	9	3	88	2.0	0.20	0.16

Note: all as %DW except COD as $mgO_2 \cdot gDW^{-1}$.

The non-calcareous nature of the system is reflected in the low $CaCO_3$ (averaging 3% DW) and high clastics (averaging 89% DW) content of the surficial sediments (cf. Auer et al. 1996). Some differences in physical-chemical character were noted among sites. For example, sediments collected from the deepest portion of the reservoir (Stations 1 and 2 in Fig. 1) were highest in VSS, COD, TOC, TN, and TP. Surficial sediments collected near the discharge of the WBDR (Station 5 and especially Station 6; Fig. 1) were also enriched in these analytes, but to a lesser extent than at Stations 1 and 2. Comparatively lower levels of VSS, TOC, TN, and TP were observed in the central part of the reservoir (Stations 3 and 4; Fig. 1). The similarity of Station 3 (Trout Creek Arm) and Station 4 (main body of the reservoir), noted here for surficial sediment composition, has been observed as well for rates of sediment deposition (Effler and Brooks, 1998) and conditions in the water column (e.g., nutrients, Effler and Bader 1998; optics, Effler et al. 1998b). Based on these observations, three coring reference sites (Stations 2, 4, and 5) were established, representing regions of potentially differing sediment character.

Sediment Oxygen Demand

Rates of SOD ($gO_2 \cdot m^{-2} \cdot d^{-1}$) determined for the three reference sites are presented (Table 4) both as measured at 8 °C rate (SOD_8) and converted ($\theta = 1.065$; Thomann and Mueller 1987) to the corresponding rate at 20 °C (SOD_{20}). Reservoir-wide, SOD_{20} ranged from 0.66 to 1.67 $gO_2 \cdot m^{-2} \cdot d^{-1}$ with a mean ± s.d. of 1.06 ± 0.23 $gO_2 \cdot m^{-2} \cdot d^{-1}$. The reproducibility of replicate measurements at a given sampling station was good (coefficient of variation, CV, ~10%) and little variation was noted between sampling dates or among locations (Fig. 4a). Analysis of variance (Tukey's test; SYSTAT 1992) indicated that differences between dates and among stations were not statistically significant, suggesting a condition of spatial and temporal homogeneity in SOD.

The paired measurements of surficial sediment COD and SOD_{20} (as averages, n = 4 for Stations 2 and 4 and n = 3 for Station 5) are consistent with the COD/SOD relationship (Fig. 5) developed from observations in Green Bay, Lake Michigan (Gardiner et al. 1984) and Onondaga Lake, NY (Gelda et al. 1995), systems

Table 4.–Results of sediment oxygen demand experiments.

Date of Core Collection, 1995	Station	# of cores [a]	# of trials [b]	Mean ± s.d. SOD_8 ($gO_2 \cdot m^{-2} \cdot d^{-1}$)	Mean ± s.d. SOD_{20} ($gO_2 \cdot m^{-2} \cdot d^{-1}$)
5-6 July	2	3	5	0.64 ± 0.09	1.36 ± 0.18
	4	3	3	0.44 ± 0.03	0.93 ± 0.06
	5	2	3	0.46 ± 0.06	0.98 ± 0.10
29-30 August	2	1	3	0.45 ± 0.07	1.04 ± 0.10
	4	1	3	0.46 ± 0.08	1.02 ± 0.17
	5	1	3	0.45 ± 0.05	0.96 ± 0.10
Overall		11	20	0.50 ± 0.11	1.06 ± 0.23

[a] total number of cores per station.

[b] total number of trials for cores collected at the same station and sampling time.

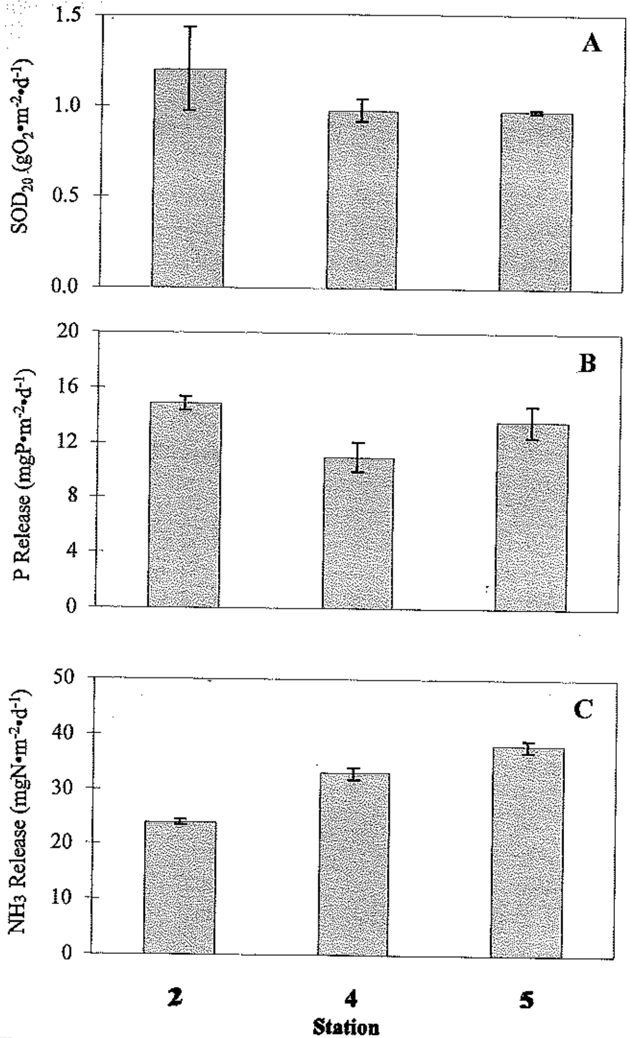

Figure 4.–Measured rates of chemical exchange: (a) sediment oxygen demand, (b) phosphorus, and (c) ammonia-nitrogen.

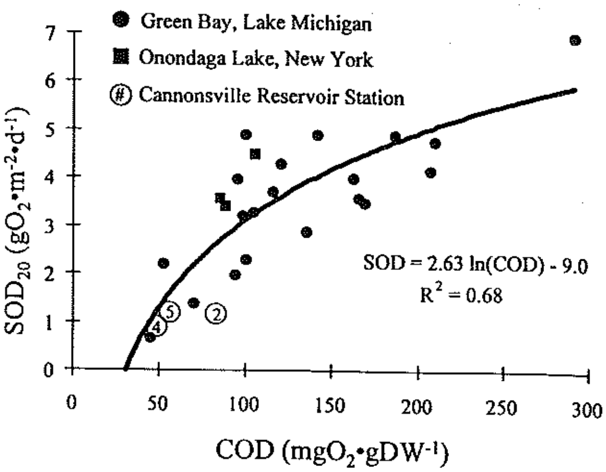

Figure 5.–The relationship between chemical oxygen demand (COD) and sediment oxygen demand (SOD).

with a trophic state comparable to that of Cannonsville Reservoir. The nonlinear nature of the COD/SOD function is a manifestation of the loss of methane to ebullition in organically enriched environments, i.e., loss of an opportunity for exertion of SOD (DiToro et al. 1990). SOD rates measured for Cannonsville Reservoir fit this relationship well, affirming the reliability of laboratory-derived SOD estimates.

Phosphorus Release

No P release was observed under aerobic conditions, and some evidence for negative uptake (P-scavenging from the water column) was noted, consistent with the observations of others (Kamp-Nielsen 1974, Penn 1994) and with the existence of a sink process for dissolved P in the reservoir's hypolimnion (as identified by Effler and Bader 1998). Anaerobic rates (Fig. 4b and Table 5) differed markedly from those measured under aerobic conditions, consistent with the Fe/P redox dynamics proposed by Mortimer (1941, 1942) and furthered by a number of researchers (e.g., Syers et al. 1973, Bostrom 1988, Golterman 1988, Penn 1994). Measured anaerobic P release rates ranged from 9.2 to 15.6 mgP · m^{-2} · d^{-1}, with a reservoir-wide mean ± s.d. of 12.9 ± 2.2 mgP · m^{-2} · d^{-1}. The reproducibility of replicate measurements of P release at a given sampling station was good (CV ~7%). Some inter-station variability was noted: mean P release rates for Station 4 were significantly lower (Tukey's test; SYSTAT 1992) than those for Stations 2 and 5. Mean P release rates for Station 2 were not significantly different from those for Station 5.

P release rates determined for Cannonsville Reservoir fall within the rather wide range (5 to 35 mgP · m^{-2} · d^{-1}) reported for eutrophic systems by Nürnberg (1988) and others (Freedman and Canale 1977, Auer et al. 1993). The large inter-lake variability in rates reported in the literature may reflect differences in sediment iron and calcium content (cf. Driscoll et al. 1993) and in redox potential at the sediment-water interface. These conditions can vary greatly due to the combined effects of the geology of the catchment basins and the trophic status of the lake (cf. Mhamdi et al. 1994). This variability further points to the need for site-specific determination of rates of sediment-P release.

Ammonia-Nitrogen Release

Substantial NH_3-N release was observed in all cores (Table 5). Rates ranged from 19.6 to 43.2 mgNH_3-N · m^{-2} · d^{-1} with a reservoir-wide mean ± s.d. of 31.8 ± 7.2 mgNH_3-N · m^{-2} · d^{-1}. Again, good

Table 5.–Results of release rate experiments.

Station	Replicate		Anaerobic NH_3-N Release ($mgN \cdot m^{-2} \cdot d^{-1}$)		Anaerobic P release ($mgP \cdot m^{-2} \cdot d^{-1}$)
2	1		30.1		15.6
	2		19.6		14.8
	3		22.2		14.4
		Mean ± S.D.	23.9 ± 4.5	Mean ± S.D.	14.9 ± 0.5
4	1		30.0		9.2
	2		32.8		9.7
	3		36.0		11.7
		Mean ± S.D.	32.9 ± 2.2	Mean ± S.D.	10.2 ± 1.1
5	1		40.4		13.0
	2		31.9		15.3
	3		43.2		12.8
		Mean ± S.D.	38.5 ± 3.9	Mean ± S.D.	13.7 ± 1.1
Overall		**Mean ±S.D.**	**31.8 ± 3.9**	**Mean ±S.D.**	**12.9 ± 2.2**

reproducibility (CV = 7 to 18%) in measurement was observed. Analysis of variance (Tukey's test; SYSTAT 1992) indicated that there was no significant difference between NH_3-N release rates measured for Stations 2 and 4, but that the rates measured for Station 2 were significantly lower than those for Station 5. A general trend of decreasing sediment NH_3-N release rates with distance from the discharge of the WBDR was noted (Fig. 4b). The NH_3-N release rates measured for Cannonsville Reservoir are of the general magnitude expected for mesotrophic systems (e.g., White Lake, Michigan, 29 to 44 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$, Freedman and Canale 1977; ELA Lake 227, Canada, 23 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$, Hesslien 1977) and are less than those reported for eutrophic lakes (Mono Lake, California, 42 to 140 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$, Jellison et al. 1993; Lake Sempach, Switzerland, 36 to 168 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$, Höhener and Gächter 1994; Onondaga Lake, New York, 78 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$, Wickman 1996).

Sediment Core Profiles

Two features stand out in the downcore profiles for TP, TN, and TOC at Stations 2, 4, and 5 (Fig. 6). First, average TP concentrations were markedly less at Station 5 (0.09% DW) than at Station 2 (0.15% DW) and at Station 4 (0.14% DW). With this exception, however, there was very little difference in the concentrations of these analytes among stations. TN levels were 0.46%, 0.47%, and 0.41% DW, and TOC levels 3.8%, 3.6% and 3.7% DW for Stations 2, 4, and 5, respectively. While these observations do suggest a certain spatial uniformity in the character of the reservoir's sediments, it is important to point out that it is the abundance of the labile fraction of the pollutant that mediates exchange, not the total pollutant concentration.

Secondly, inspection of the sediment core profiles reveals information about the tendency of particulate N, P, and organic carbon to participate in diagenesis, i.e., conversion to the soluble form with subsequent release to the overlying water. In sediments that receive a relatively constant input of particulate matter, diagenesis is evidenced by downcore reduction in concentration. This is most clearly illustrated in the TN and TOC profiles for Station 4 (Fig. 6), but is in evidence as well for TN and TOC at the other stations. There is little evidence for the occurrence of diagenesis in the TP profiles. This interpretation is consistent with field observations of hypolimnetic DO depletion (SOD exertion; carbon diagenesis), accumulation of NH_3-N in the hypolimnion following deoxygenation (N diagenesis) and the absence of significant hypolimnetic accumulation of phosphorus (P diagenesis; Effler and Bader 1998). Laboratory measurements of chemical exchange support these concepts as well: significant NH_3-N release and SOD were observed, but no P release was noted (under aerobic conditions). Iron reduction and the attendant P release would not be

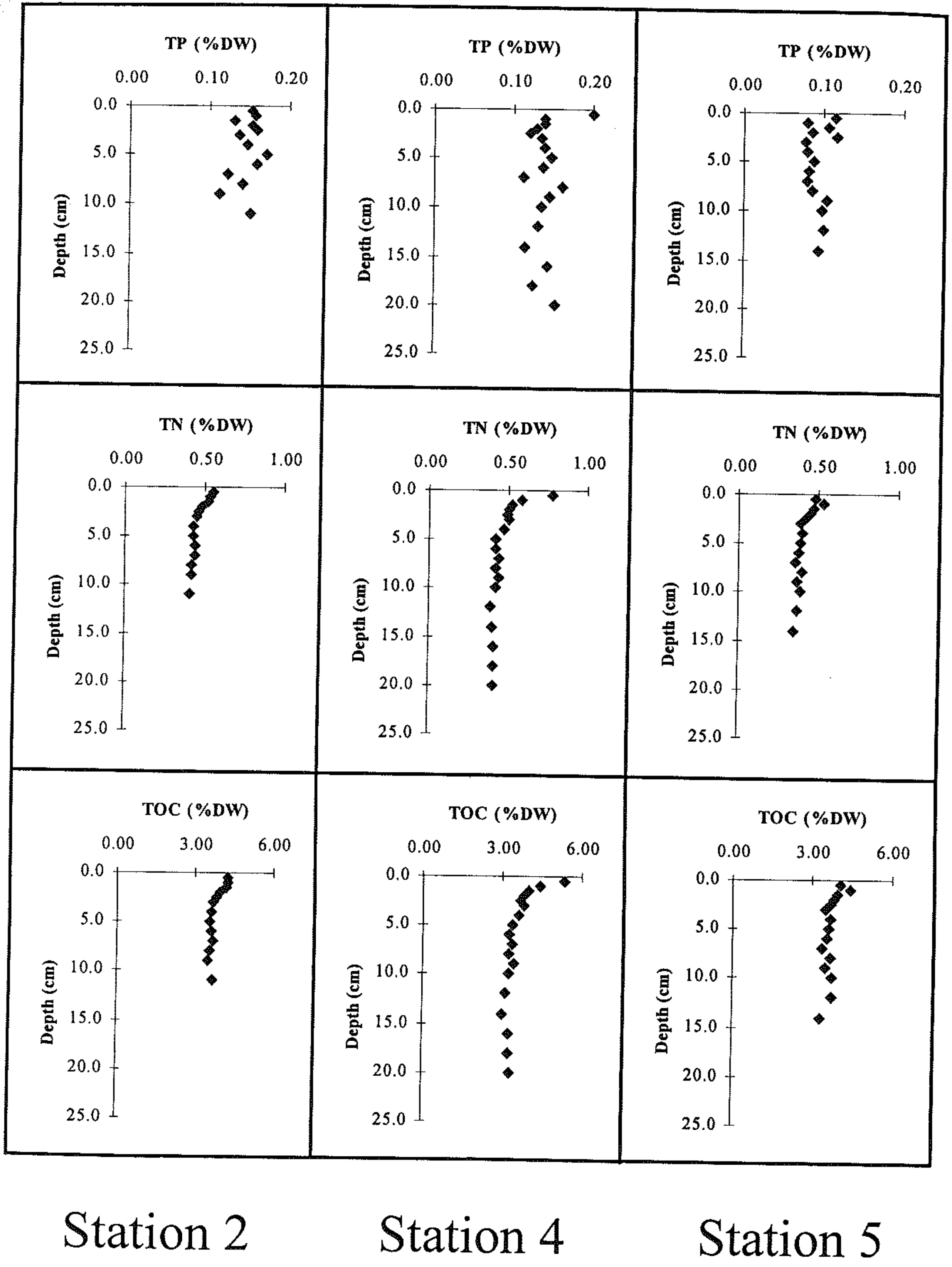

Figure 6.–Sediment profiles of TN, TP, and TOC for three stations on Cannonsville Reservoir.

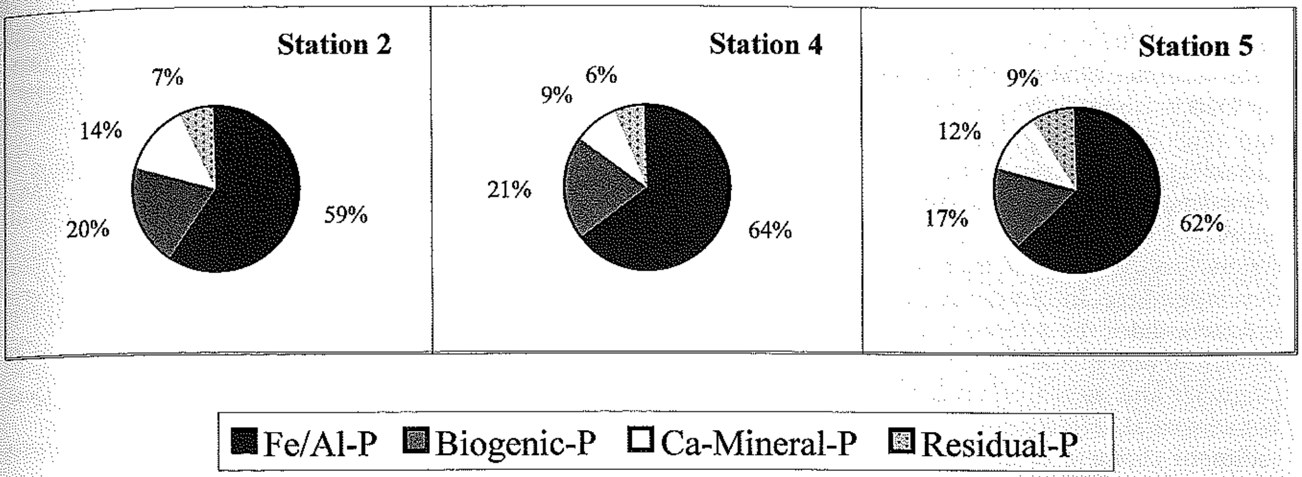

Figure 7.–Operationally-defined phosphorus fractions for sediments from three stations on Cannonsville Reservoir.

expected until the more thermodynamically favored electron acceptors (O_2, Mn^{2+}, and NO_3^-) are depleted. The lower waters of the hypolimnion are anaerobic by midsummer and the NO_3^- pool is partially depleted (but not eliminated) by turnover and thus P release is not expected (Effler and Bader 1998). Despite the fact that P release does not occur to any great extent at present, there is considerable potential for release if redox conditions in the hypolimnion change in the future. Chemical extraction measurements conducted on cores from Stations 2, 4, and 5 (Fig. 7) show Cannonsville Reservoir sediments to be rich in those P-fractions known to undergo diagenesis (Fe/Al-P and biogenic-P; Penn et al. 1995). Further eutrophication of this system (additional P loads), leading to higher rates of hypolimnetic DO depletion, could markedly alter the P release regimen, making this internal input potentially important to the overall rates of P loading and cycling.

Summary and Application

A surficial sediment survey, laboratory measurements of chemical exchange at the sediment-water interface, and studies of sediment chemical profiles were conducted on Cannonsville Reservoir. The surficial sediment survey identified three regions that apparently differed in their levels of enrichment in TN, TP, and TOC. Enriched areas were found proximate to the discharge of the WBDR (the reservoir's major tributary) and in a depositional basin located adjacent to the reservoir's dam. Sediments in the middle portion of the reservoir had lower levels of TN, TP, and TOC.

Sediment-water exchange rates determined for Cannonsville Reservoir included SOD and P and NH_3-N release. The SOD_{20} measured for the reservoir (average = 1.06 ± 0.23 $gO_2 \cdot m^{-2} \cdot d^{-1}$) falls within the range of values reported for other productive systems and is in agreement with values predicted using an SOD/COD relationship developed from observations reported for two other systems of comparable trophic state. Rates of NH_3-N (average = 31.8 ± 7.2 $mgNH_3\text{-}N \cdot m^{-2} \cdot d^{-1}$) and anaerobic P release (12.9 ± 2.2 $mgP \cdot m^{-2} \cdot d^{-1}$) were consistent with those reported from the literature for systems with comparable levels of water column nutrient enrichment and productivity.

Little variation was observed in the TP, TN, and TOC profiles developed using cores from the three reference stations. This stands in contrast to the findings of the surficial sediment survey where horizontal heterogeneity in sediment enrichment was noted with position in the reservoir. One exception to this was the markedly lower TP concentrations observed in sediments proximate to the discharge of the WBDR. Chemical fractionation analyses indicated that Cannonsville Reservoir sediments are rich in labile particulate P and have the potential to support significant rates of P release, a conclusion consistent with the results of laboratory measurements of anaerobic P release. This is of potential significance to future water quality conditions in the reservoir should trophic state conditions further deteriorate. Applying the measured averaged anaerobic sediment-P flux of 12.9 $mgP \cdot m^{-2} \cdot d^{-1}$ over a sediment-water interface of 1.3×10^7 m^2 (July 1995) would yield an internal P loading of 16.8 $kg \cdot d^{-1}$, approximately one-third of the external load contributed by WBDR over the April-October period.

Results such as those presented here may be of considerable value in supporting the development of water quality models used to guide lake and reservoir restoration efforts. Chemical exchange at the sediment-water interface can be a dominant source/sink term in the mass balance for oxygen, nitrogen, and phosphorus and rates of exchange may demonstrate significant variability both among and within systems. Concerns regarding intersystem variability in rates may be addressed by obtaining high quality (reproducible), system-specific chemical exchange rates such as those developed here. Intrasystem variability in rates may be accommodated by adopting a model segmentation consistent with spatial differences in surficial sediment character and measured rates of chemical exchange. Some spatial heterogeneity was noted in surficial sediment characteristics over the reservoir, however this was not borne out by sediment core profiles. Of most importance from a modeling perspective, few significant differences in exchange rates were noted among stations. Thus reservoir-wide rates may be reliably utilized in one-dimensional model applications. Exceptions to this lack of variation include a (statistically significant) lower P release rate at Station 4 compared with Stations 2 and 5 and a (statistically significant) lower NH_3-release rate at Station 2 compared with Station 5. Considerable confidence is vested in the values obtained for individual stations because of the good reproducibility of replicate measurements. Thus it is recommended that station-specific values be retained in two- and three-dimensional model applications. Sensitivity analysis may be used to determine the importance of the level of spatial resolution of the model to the successful simulation of water column conditions. Should the model prove sensitive to the variation in measured released rates over the range reported here, it is recommended that additional sampling/analysis be conducted to improve the spatial resolution of release rates.

ACKNOWLEDGMENTS: The authors wish to thank Mary J. Babiera for her assistance in developing sediment phosphorus profiles. This research was supported by a grant from the New York City Department of Environmental Protection through the Upstate Freshwater Institute. This is Contribution No. 175 of the Upstate Freshwater Institute.

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